Observational constraints on the chemistry of isoprene nitrates over the eastern United States

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Abstract

We use chemical transport model simulations in conjunction with observations over the eastern United States from the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign during summer 2004 to constrain uncertainties in the chemistry of isoprene nitrates. The best agreement between simulated and observed boundary layer concentrations of organic nitrates are obtained with a 4% yield of isoprene nitrate production from the reaction of isoprene hydroxyperoxy radicals with NO, recycling of 40% NO_x when isoprene nitrates react with OH, and fast dry deposition of isoprene nitrates. We also identify a range of other plausible values for these parameters, based on other simulations showing reasonable agreement with observations. We find that ~50% of the isoprene nitrate production occurs via reactions of isoprene (or its oxidation products) with the NO_3 radical. Isoprene nitrates are shown to have a major impact on the nitrogen oxide ($NO_x = NO + NO_2$) budget in the U.S. continental boundary layer, consuming 17-21% of the emitted NO_x, with 3-6% being recycled back to NO_x and the remainder being exported as isoprene nitrates (10-13%) or deposited (10-13%).

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1. Introduction

Photochemical oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x = NO + NO_2) contributes to the production of ozone. Over the eastern United States during summer, chemical reactivity and ozone production are dominated by biogenic VOCs, particularly isoprene (2-methyl-1,3-butadiene), rather than anthropogenic VOCs [e.g., *Trainer et al.*, 1987]. Isoprene oxidation also modulates the partitioning and fate of reactive nitrogen within the continental boundary layer [e.g., *Horowitz et al.*, 1998; *Houweling et al.*, 1998]. Recent modeling studies have demonstrated that ozone concentrations and reactive nitrogen partitioning are sensitive to uncertainties in the isoprene chemical oxidation pathways [*Horowitz et al.*, 1998; *von Kuhlmann* et al., 2004; *Fiore* et al., 2005; *Wu et al.*, 2006].

Specific uncertainties include the magnitude and spatial distribution of isoprene emissions, the yield and fate of isoprene nitrates, and the fate of organic hydroperoxides. Previous studies suggest that ozone is only weakly sensitive to the uncertainties in organic hydroperoxides (up to 2-3 ppbv), while the choice of isoprene emissions inventory can have large local or regional effects on ozone (up to 15 ppbv locally) [*von Kuhlmann et al.*, 2004; *Fiore et al.*, 2005]. We focus in this paper on the uncertainties concerning isoprene nitrates, which have been shown to affect surface ozone strongly, by up to 10 ppbv [*von Kuhlmann et al.*, 2004; *Fiore et al.*, 2005]. We use chemical transport model simulations in conjunction with observations from a recent field campaign to constrain the uncertainties in isoprene nitrate chemistry and examine the implications of these constraints for the NO_x budget.

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When isoprene is oxidized by OH, six different isomeric hydroxyperoxy (RO_2) radicals are formed (after the addition of O_2). Under high-NO_x conditions these radicals typically react with NO, forming primarily hydroxalkoxy (RO) radicals with a minor channel leading to the production of organic hydroxynitrates ($RONO_2$, "isoprene nitrates") [e.g., *Chen et al.*, 1998]. The chemistry of these isoprene nitrates can strongly influence ozone and NO_x in high-isoprene regions [e.g., *Horowitz et al.*, 1998; *von Kuhlmann et al.*, 2004; *Fiore et al.*, 2005], but is highly uncertain. Laboratory studies have estimated the yield of isoprene nitrates from the RO_2+NO reaction to range from 4.4% to 15% [*Chen et al.*, 1998; *Tuazon and Atkinson*, 1990 (corrected as discussed by *Paulson et al.*, 1992); *Chuong and Steven*, 2002; *Sprengnether et al.*, 2002]. Model studies have shown that tropospheric ozone production and surface concentrations are sensitive to the isoprene nitrate yield [*von Kuhlmann et al.*, 2004; *Wu et al.*, 2006].

Organic nitrates are also formed via the nighttime oxidation of isoprene by NO_3, which proceeds by addition of NO_3 to one of the double bonds in isoprene followed by addition of O_2 to form nitrooxyalkyl peroxy radicals. These radicals can then undergo subsequent reactions to form stable organic nitrates, or can decompose to release NO_x; the relative amounts of organic nitrates versus released NO_x are poorly known [e.g., *Paulson and Seinfeld*, 1992; *Fan and Zhang*, 2004]. The importance of the isoprene-NO_3 channel versus the isoprene-OH channel for isoprene nitrate production is also uncertain, but a modeling study suggests that > 60% of isoprene nitrates may be produced through the isoprene-NO_3 pathway [*von Kuhlmann et al.*, 2004].

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Isoprene nitrates contain a double bond, so they are still highly reactive towards OH, but the reaction rate and products formed from this reaction are uncertain. The reaction rate constant for isoprene nitrates + OH have been estimated to range from $(1.3-9) \times 10^{-11}$ molec^{-1} cm^3 s^{-1} [*Paulson and Seinfeld*, 1992; *Chen et al.*, 1998; *Giacopelli et al.*, 2005], while some model studies have assumed rate constants as low as 6.8×10^{-13} [*Brasseur et al.*, 1998].

The products of the isoprene nitrate + OH reaction have not been directly measured. *Paulson and Seinfeld* [1992] suggested that this reaction should release NO$_x$, while other studies suggest that the reaction of some isomers will lead to the production of secondary multifunctional organic nitrates [*Grossenbacher et al.*, 2001; *Giacopelli et al.*, 2005]. The release of NO$_x$ by this reaction or its continued sequestration in organic nitrates can significantly alter the extent to which isoprene chemistry acts as a sink for NO$_x$ [e.g., *Chen et al.*, 1998; *Horowitz et al.*, 1998], with up to ~10% effects on surface ozone concentrations [*von Kuhlmann et al.*, 2004].

Removal of isoprene nitrates by wet and dry deposition provides a permanent sink for atmospheric NO$_x$. The dry deposition velocity of isoprene nitrates has been estimated to range from that of PAN (0.4-0.65 cm/s) [*Shepson et al.*, 1996; *Giacopelli et al.*, 2005] to that of HNO$_3$ (4-5 cm/s) [*Rosen et al.*, 2004]. The rate of wet deposition depends on the Henry's law constant, which has been estimated by analogy with comparable species, to range from $H(298K) = 6.0 \times 10^3$ M/atm [*Shepson et al.*, 1996] to 1.7×10^4 [*von Kuhlmann et al.*, 2004]. Based on these estimates, and assumed reaction rates with OH, *Shepson et al.* [1996] predicted that reaction with OH should be the dominant loss process for isoprene nitrates, with an atmospheric lifetime of ~18h.

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The International Consortium for Atmospheric Research on Transport and Transformation (ICARTT), a multi-agency international field campaign conducted during summer 2004, measured isoprene, its oxidation products, reactive nitrogen compounds, and ozone over the eastern United States. Since chemistry in this region and season is strongly affected by emissions of both biogenic isoprene and anthropogenic NO_x, the ICARTT campaign presents an opportunity to study the effect of isoprene on reactive nitrogen partitioning and ozone production. The objective of this paper is to analyze the ICARTT observations in conjunction with our 3-dimensional chemical transport model simulations to provide new constraints on the chemistry of isoprene nitrates. The model configuration is described and the results are evaluated with observations in Section 2. We discuss the isoprene nitrates simulated in our standard model configuration and several sensitivity runs in Section 3. In Section 4, we derive constraints on the chemistry of isoprene nitrates, and examine the implications of these constraints for the NO_y budget. Conclusions are presented in Section 5.

2. Model description and evaluation

2.1 Model description

We simulate conditions during the ICARTT period (July-August 2004) using the MOZART-4 chemical transport model [*Emmons et al.*, 2006, manuscript in preparation]. This model is an updated version of the MOZART-2 model described by *Horowitz et al.* [2003] with

aerosol chemistry based on that of *Tie et al.* [2005]. Model updates relevant to our study are described below. Photolysis rates are calculated interactively to account for absorption and scattering by aerosols and clouds using Fast-TUV [*Madronich and Flocke*, 1998; *Tie et al.*, 2005]. The influx of O_3 from the stratosphere is prescribed using the SYNOZ technique (500 Tg yr^{-1}) [*McLinden et al.*, 2000]. The prescribed monthly mean deposition velocities for O_3 and PAN have been increased based on those used by *Bey et al.* [2001]. The chemistry of higher alkanes is represented by "bigalk" (C_5H_{12}), a lumped species representing the butanes, pentanes, and hexanes, while that of higher alkenes is represented by "bigene" (C_4H_8), a lumped species representing mostly 2-methylpropene and 2-butene. An additional new species, "toluene" (C_7H_8), is a lumped aromatic compound representing mostly benzene, toluene, and the xylenes. Additional oxidation products of the above species have also been added. The oxidation scheme for terpenes (represented by α-pinene) has been updated to reflect recent laboratory data. The updates to the chemistry in MOZART-4 are more fully described by *Emmons et al.* [2006].

The isoprene oxidation mechanism is our BASE simulation is shown in Table 1. The treatment of isoprene nitrates has been modified from that in MOZART-2 [*Horowitz et al.*, 2003]. In particular, we add a new species (XNITR in Table 1) to represent secondary multifunctional organic nitrates. The reaction of primary isoprene nitrates (ONITR) with OH recycles 40% of NO_x, rather than 100% as in MOZART-2, with the balance forming XNITR based on recent studies suggesting that this reaction produces some secondary nitrates [e.g., *Grossenbacher et al.*, 2001; *Giacopelli et al.*, 2005]. XNITR has no chemical losses in our mechanism, as its further reactions are assumed to convet it to more highly substituted organic nitrates. The reaction ONITR + NO_3 is also assumed to produce XNITR. The yield of ONITR

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from the addition branch of the ISOPO2 + NO reaction has been decreased from 8% in MOZART-2 to 4% [e.g., *Chen et al.*, 1998] in the BASE simulation. We assume that terpene oxidation also produces ONITR, with an 18% yield from the reaction of terpene peroxy radicals with NO [*Nozière et al.*, 1999]. In Section 3, we evaluate the sensitivity of our results to the assumptions in our BASE isoprene mechanism, using the additional model simulations described in Table 2.

Global emissions were specified as by *Horowitz et al.* [2003], with anthropogenic emissions based on EDGAR v2.0 [*Olivier et al.*, 1996] and biomass burning from *Müller* [1992] and *Hao and Liu* [1994] with emission ratios from *Andreae and Merlet* [2001]. Isoprene and monoterpene emissions are calculated interactively based on temperature, sunlight, and vegetation type using algorithms from MEGAN v.0 [*Guenther et al.*, 2006]. Over North America during summer, we use anthropogenic surface emissions based on the EPA National Emissions Inventory (NEI99, version 3) [S. McKeen, personal communication, 2004], and the daily biomass burning emission inventory developed by *Turquety et al.* [2006].

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Meteorological fields are provided by the NCEP Global Forecast System (GFS) every three hours. The model resolution is 1.9° latitude x 1.9° longitude, with 64 vertical levels, and a dynamical and chemical timestep of 15 minutes. The BASE model simulation was conducted from December 2003 through the ICARTT period (July-August 2004). Sensitivity simulations (Section 3.2) begin in May 2004, allowing for a two-month spinup period sufficient to capture changes in summertime continental boundary layer chemistry.

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2.2 Evaluation with ICARTT observations

We evaluate the results of the MOZART-4 BASE simulation with observations made on board the NASA DC-8 and NOAA WP-3D aircraft during ICARTT. Simulated concentrations are sampled every minute along the flight tracks of the two aircraft and then averaged onto the model grid for each flight. Comparisons of isoprene, isoprene oxidation products, ozone, and ozone precursors below 2km in the eastern United States are presented in Figure 1. Isoprene concentrations show little bias, but are poorly correlated with observations ($r^2 = 0.08$ and mean bias = +18% for NASA, $r^2 = 0.30$ and bias = -12% for NOAA), most likely due to the short lifetime of isoprene and the high spatial variability of its emissions. The first generation isoprene oxidation products methylvinyl ketone and methacrolein, which have longer atmospheric lifetimes, are better simulated by the model ($r^2 = 0.49$, bias = -7%), suggesting that the isoprene emissions estimated in the model using MEGAN reasonably simulate the large-scale spatial and temporal distribution of isoprene emissions.

Concentrations of NO_x and CO are moderately well correlated with observations ($r^2 = 0.41$ and 0.14 for CO from NASA and NOAA, respectively, $r^2 = 0.37$ for NO_x from NASA), with an average model overestimated of 35-45%. Secondary oxidation products are reasonably well simulated by the model. Formaldehyde (CH_2O) and PAN concentrations are well correlated with the observations, but PAN tends to be overestimated in the boundary layer. PAN concentrations in the free troposphere have little mean bias (not shown). Concentrations of HNO_3 and H_2O_2 are poorly correlated with observations, suggesting possible model errors in wet

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deposition. Ozone is slightly overestimated (mean bias = +9.6%) and is moderately well correlated with observations ($r^2 = 0.31$).

The agreement between simulated and observed concentrations of the species evaluated in this section is relatively insensitive to assumptions about isoprene nitrate chemistry, and does not differ significantly in the sensitivity simulations (Section 3.2) from the comparisons shown here for the BASE case. However, the comparisons between simulated and observed organic nitrate concentrations vary strongly in the sensitivity simulations. Thus, those comparisons are deferred until Section 4.1, where they are used to provide constraints on the chemistry of isoprene nitrates.

3. Isoprene nitrate budgets

3.1 Budget in base case

Budgets for isoprene nitrate production and loss in the eastern United States boundary layer during July 2004 are presented in Figure 2. In the BASE simulation, half of the isoprene nitrate production occurs through the NO_3 pathway, in which isoprene reacts with NO_3 to ISOPNO3, which can then react with NO, NO_3, or HO_2 to form ONITR (see Table 1). All ISOPNO3 reaction pathways are assumed to form ONITR with a yield of 79.4% [*Horowitz et al.*, 2003]. The large contribution of this pathway to isoprene nitrate production, despite the small fraction of isoprene oxidized via this pathway, agrees well with the findings of *von Kuhlmann et*

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al. [2004]. About 25% of the isoprene nitrate production occurs via the reaction ISOPO2 + NO, which produces ONITR with a 4% yield in this simulation, with 12-14% each coming from the reactions MACRO2+NO and TERPO2+NO (TERPO2 is formed by terpenes+OH or terpenes+NO$_3$). The loss of isoprene nitrates in the BASE simulation occurs largely by dry deposition (44%) and reaction with OH (26%), with minor losses by transport (17%) and wet deposition (14%).

3.2 Sensitivity simulations

In this section, we examine the sensitivity of our model budgets to assumptions concerning the production and loss of isoprene nitrates, using the additional simulations in Table 2. In particular, we examine the model sensitivity to isoprene nitrate: yield, OH reaction rate, recycling of NO$_x$, and deposition rate.

The production of isoprene nitrates following the oxidation of isoprene by OH depends on the yield of these nitrates from the reaction of the isoprene peroxy radicals (ISOPO2 in Table 1) with NO. We conduct sensitivity simulations in which the yield is increased from the BASE case value of 4% [*Chen et al.*, 1998] to 8%, as assumed by *Fan and Zhang* [2004]. In the simulations with an 8% yield (8% and 8%_slowOH in Table 2), the production of isoprene nitrates via the ISOPO2+NO pathway doubles compared to the runs with a 4% yield (BASE and 4%_slowOH), but production via other pathways is relatively unchanged. Thus, the total production of isoprene nitrates increases by ~22% in these simulations.

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The chemical loss of isoprene nitrates (ONITR) is primarily through reaction with OH. Our BASE simulation assumes a rate constant of k = 4.5×10^{-11} molec^{-1} cm^3 s^{-1} for isoprene nitrates + OH [*Emmons et al.*, 2006], within the range of $(3-9) \times 10^{-11}$ molec^{-1} cm^3 s^{-1} estimated by *Giacopelli et al.* [2005] using the method of *Kwok and Atkinson* [1995]. There is evidence that the *Kwok and Atkinson* [1995] method may overestimate the rate constant for OH reaction with hydroxyalkyl nitrates by a factor of 2-21 [*Neeb*, 2000; *Treves and Rudich*, 2003], so we also consider a lower rate constant of k = 1.3×10^{-11} molec^{-1} cm^3 s^{-1} (simulations 4%_slowOH, 8%_slowOH), similar to that used in several other studies [*Shepson et al.*, 1996; *Chen et al.*, 1998; *Pöschl et al.*, 2000; *Horowitz et al.*, 2003]. The ONITR+OH reaction accounts for 26% of the isoprene nitrate loss when a fast reaction rate is assumed (BASE and 8%), but only ~21% when a slower rate is used (4%_slowOH and 8%_slowOH).

When isoprene nitrates (ONITR) react with OH, the reactive nitrogen can be recycled to NO_x or retained as XNITR. In the BASE case, we assume a NO_x recycling efficiency of 40%. Since this recycling efficiency is uncertain [*Paulson and Seinfeld*, 1992; *Chen et al.*, 1998; *Grossenbacher et al.*, 2001, *Giacopelli et al.*, 2005], we include three sensitivity simulations in which the recycling is varied from extreme values of 0% (4%_0%NOx in Table 2) to 100% (4%_100%NOx and 8%_slowOH_100%NOx). When the recycling is completely turned off, the ONITR+OH reaction ceases to be a sink for isoprene nitrates. As a result, losses via dry and wet deposition increase by ~30% and ~40%, respectively. When the recycling is increased from 40% to 100%, the loss of isoprene nitrates from ONITR+OH increases proportionally by a factor of 2.5, and accounts for 50-64% of the total loss.

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The final sensitivity we examine is the rate at which isoprene nitrates (ONITR and XNITR) are lost by deposition. In the BASE simulation, we assume that isoprene nitrates deposit rapidly, with a dry deposition velocity equal to that of HNO_3 and a wet deposition rate (Henry's Law constant of $H_{298} = 7.51x10^3$ M atm^{-1}) similar to that assumed by *Shepson et al.* [1996]. Since dry deposition dominates over wet deposition as a loss pathway from the boundary layer (see Section 3.1), we examine the sensitivity of our results to the removal rate by decreasing the dry deposition velocity of isoprene nitrates to that of PAN (simulations 4%_slowDD, 8%_slowDD) [*Shepson et al.*, 1996; *Giacopelli et al.*, 2005]. In these simulations with slow dry deposition, the ONITR+OH reaction increases in importance, accounting for up to 34% of the isoprene nitrate loss.

4. Constraints from observations

4.1 Isoprene nitrate evaluation

The sensitivity simulations described above (Section 3.2 and Table 2) most dramatically affect the simulated concentrations of isoprene nitrates, with only small impacts on the other species evaluated in Section 2.2. In this section, we utilize measurements of total alkyl nitrates (ΣAN) [Cohen references] during ICARTT to constrain the plausible ranges for the isoprene nitrate production and loss processes considered. In the model, isoprene nitrates are the dominant contributors to ΣAN. The speciated (non-isoprene) alkyl nitrates measured during ICARTT

[*Blake et al.*, xxxx] typically account for an average of only ~10% of the observed ΣAN,

indicating that ΣAN is primarily composed of isoprene nitrates, as suggested by the model.

Simulated organic nitrate concentrations (ONITR + XNITR + ISOPNO3 + other organic

nitrates) are compared with observations of ΣAN in Figure 3. The mean organic nitrates

simulated in the BASE case agree well with observed concentrations in the boundary layer (+10-

15% bias), but underestimate free tropospheric concentrations by more than a factor of 2.

Similarly, the BASE case reproduces the observed ΣAN:ozone correlation slope (12.2 simulated

and observed), although the correlation is much stronger in the model (r=0.87 vs. 0.35 observed).

The 8% simulation overestimates both ΣAN (+40% bias) and the ΣAN:ozone slope (15.9).

The simulations with slower loss of ONITR via OH (4%_slowOH and 8%_slowOH)

have 10% higher concentrations of ΣAN than the corresponding simulations with the faster

ONITR+OH reaction rate, even though the reaction rate constant was decreased by more than a

factor of 3. This small response indicates that reaction with OH is a relatively small loss of

isoprene nitrates compare with deposition, as demonstrated by the isoprene nitrate budgets in

Section 3. The higher concentrations of ΣAN increase the correlation slope ΣAN:ozone,

degrading agreement with observations.

When we decrease the dry deposition velocity of isoprene nitrates from that of HNO_3 to

that of PAN (simulations 4%_slowDD and 8%_slowDD), ΣAN concentrations increase by

approximately a factor of 2, dramatically worsening agreement with observed ΣAN

concentrations and correlation slopes ΣAN:ozone in the boundary layer; simulated

concentrations of ΣAN in the free troposphere approach observed values, but are still slightly underestimated. The discrepancy between simulated and observed ΣAN in the free troposphere is discussed further in Section 4.2.

In the final set of sensitivity simulations, the recycling efficiency of NO_x from the reaction of ONITR+OH is varied. When all of the NO_x is recycled (4%_100%NOx), the boundary layer concentrations of ΣAN are underestimated by a factor of 4 or more. If we additionally assume an 8% yield of ONITR and the slow rate of ONITR+OH reaction, the ΣAN concentrations increase to 50-65% of observed values, but the ΣAN:ozone correlation slope is still greatly underestimated (7.4). In both of the simulations with 100% recycling (4%_100%NOx, 8%_slowOH_100%_NOx), the free tropospheric ΣAN concentrations are dramatically underestimated by a factor of 10 or more. On the other hand, if the ONITR+OH reaction is assumed to recycle no NO_x (4%_0%NOx), instead forming XNITR exclusively, ΣAN concentrations increase by 50% from the BASE case, leading to 60-70% overestimates of observed ΣAN and ΣAN:ozone.

Based on the comparisons with observed ΣAN and ΣAN:ozone, we find that the BASE simulation — with its 4% yield of isoprene nitrates from ISOPO2+NO, fast rate of reaction of isoprene nitrates with OH recycling 40% NO_x, and fast loss by dry deposition — best matches observations of ΣAN concentrations and ΣAN:ozone correlation slopes. The simulations with an 8% yield and/or slower reaction of ONITR+OH degrade agreement with observation somewhat. The simulations with slow dry deposition and with either 0% or 100% NO_x recycling show the worst agreement with observations. Based on the quality of agreement with observations, we

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select the BASE case as the "best guess" set of model parameters, but also consider a range of uncertainty including the other simulations showing reasonable agreement with observations (4%_slowOH, 8%, 8%_slowOH).

Our best guess of a 4% yield of isoprene nitrates agrees well with the values measured by *Chen et al.* [1998], but is significantly lower than that from other studies [*Tuazon and Atkinson*, 1990; *Chuong and Steven*, 2002; *Sprengnether et al.*, 2002]. The BASE case ONITR+OH rate constant of $k=4.5\times10^{-11}$ molec^{-1} cm^3 s^{-1} is within the range estimated by *Giacopelli et al.* [2005], but we find that the agreement with observations is only slightly degraded when the lower reaction rate of $k=1.3\times10^{-11}$ is used (e.g., *Paulson and Seinfeld*, 1992; *Chen et al.*, 1998). We find that the assumption of 40% NO_x recycling from ONITR+OH gives the best agreement with observations, although a somewhat higher recycling rate could be supported, especially if the production yield of isoprene nitrates were higher. The degree of recycling has not been well constrained by previous studies, with *Paulson and Seinfeld* [1992] arguing that NO_x should be released from this reaction, but other studies suggesting the formation of secondary multifunctional nitrates [*Grossenbacher et al.*, 2001; *Giacopelli et al.*, 2005]. Finally, our results suggest that isoprene nitrates are removed relatively quickly by dry deposition, as supported by observations by *Rosen et al.* [2004], but faster than suggested by [*Shepson et al.*, 1996; *Giacopelli et al.*, 2005].

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4.2 Budget implications

Considering all of the sensitivity simulations in Table 2, we find that the formation of isoprene nitrates has a large effect on the NO_x budget in the summertime boundary layer. Out of a total 519 GgN emitted from the eastern United States in July, 88-111 GgN (17-21%) cycles through isoprene nitrates depending on the assumed yield from ISOPO2+NO. Once formed, 0-58 GgN (0-11% of emissions) is recycled from isoprene nitrates back to NO_x within the continental boundary layer, 24-67 GgN (5-13% of emissions) are removed permanently by dry and wet deposition, and 6-44 GgN (1-8% of emissions) are exported to the free troposphere as isoprene nitrates.

The ranges above can be narrowed significantly by limiting consideration to those simulations that agree best with ΣAN and ΣAN:ozone observations (Figure 3), eliminating the simulations with slow dry deposition and with 0% and 100% NO_x recycling. The constrained budgets still include nearly the full range of isoprene nitrate production rates (88-109 GgN), but limit the loss terms to 18-29 GgN recycled to NO_x, 51-67 GgN deposited, and 15-19 GgN exported. The BASE simulation, which agrees most closely with observations, suggests "best guess" values for these budget terms of: isoprene nitrate production (89 GgN, 17% of NO_x emissions), recycling to NO_x (23 GgN, 4%), deposited (51 GgN, 10%), and exported (15 GgN, 3%).

Isoprene nitrate chemistry affects ozone concentrations through its impact on the NO_x budget. The mean ozone mixing ratios in the boundary layer change from their BASE case

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values (Figure 1) by up to +2.9 ppbv (in simulation 4%_100NOx) and -1.8 ppbv (4%_0NOx), demonstrating that recycling of NO_x recycling from isoprene nitrates can have almost a 5 ppbv impact on ozone. If we consider only the constrained simulations, the range of mean ozone perturbations decreases to -1.8 to 0 ppbv.

Most of the analysis in this paper has focused on the chemistry of the continental boundary layer, where isoprene is expected to most strongly impact the chemistry and isoprene nitrates are expected to dominate ΣAN. In the boundary layer, we find that the BASE simulation best reproduces ICARTT observations, particularly of ΣAN concentrations and ΣAN:ozone correlations. All of the simulations presented here, however, considerably underestimate ΣAN in the free troposphere. The simulations that most closely match the free tropospheric observations (4%_slowDD and 8%_slowDD; mean bias of -40% and -25%, respectively) overestimate ΣAN and the ΣAN:ozone correlation slope by factors of 2-3 in the boundary layer. The simulations with 100% NOx recycling from ONITR+OH (4%_100%NOx and 8%_slowOH_100%NOx), which underestimate ΣAN in the boundary layer by a factor of ~2 or more, underestimate free tropospheric concentrations by a factor of 10 or more, indicating that most of the organic nitrates in the model in the free troposphere are secondary multifunctional organic nitrates (XNITR). The underestimate of ΣAN in all simulations is likely due to other sources of organic nitrates in the free troposphere not represented in the model. The speciated alkyl nitrates measured during ICARTT [*Blake et al.*, xxxx], however, typically account for only ~10% of the observed ΣAN, even in the free troposphere. Alternatively, the underestimate could be caused by insufficient vertical mixing out of the boundary layer in the model, which could also account for the model overestimate of NO_x and CO in the boundary layer. While increased boundary layer ventilation

would decrease isoprene nitrate concentrations in the boundary layer, it would not be expected to have a strong effect on the simulated ratio ΣAN:ozone, suggesting that our selection of a "best guess" simulation (Section 4.1) should be robust to a possible model bias in ventilation.

5. Conclusions

We combine model simulations and observations from the ICARTT field campaign over the eastern United States during summer 2004 to constrain the chemistry of isoprene nitrates. Trace species concentrations simulated by our model generally agree well with observations, although continental boundary layer concentrations of NO_x and CO tend to be overestimated by 35-45%, and PAN by a factor of ~2; free tropospheric concentrations of these species do not show this overestimate. Additional simulations are conducted to examine the sensitivity of model results to assumptions about the following uncertain aspects of isoprene chemistry: isoprene nitrate production yield, chemical loss rate, NO_x recycling, and dry deposition. Observed concentrations of total alkyl nitrates (ΣAN) and the correlation of ΣAN with ozone are used to constrain the possible values of the above parameters. We find that our simulations with low deposition velocities for isoprene nitrates produce unacceptably high boundary layer concentrations of isoprene nitrates. Extreme rates of NO_x recycling (0% or 100%) from the reaction of isoprene nitrates with OH lead to isoprene nitrate concentrations that are strongly biased (high or low, respectively) compared with observations, but model results are relatively insensitive to the rate of this reaction. Finally, better agreement is obtained with a lower isoprene nitrate production yield of 4% than with a higher yield of 8%. The observations are best reproduced by the BASE simulation, which matches the mean observed ΣAN concentrations in

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the boundary layer within 10-15%, and the observed ΣAN:ozone correlation slope (12.2 in the model and observations).

Based on the evaluation of model results versus observations, we find that the most likely values for the parameters considered are: an isoprene nitrate yield from ISOPO2+NO of 4%, recycling of about half of ONITR to NO_x in the reaction with OH, and fast removal of isoprene nitrates by dry deposition (at a rate similar to that of HNO_3). We also identify a range of plausible values for these parameters based on other simulations that show reasonable agreement with observations (4%_slowOH, 8%, 8%_slowOH). That is, an 8% yield of isoprene nitrates or a slower loss of isoprene nitrates by reaction with OH slightly degrade agreement with observations, but cannot be ruled out by this study. Of course, the set of sensitivity experiments conducted here are not exhaustive of all possible values and combinations of the parameters studied and it is possible that other combinations of values, such as an 8% production yield of ONITR from ISOPO2+NO together with a somewhat higher rate of NO_x recycling from ONITR+OH, would match observational constraints as well as the BASE simulation.

We find that the NO_3 production pathway accounts for 50% of the total organic nitrate production in the BASE case (with a range of ~40-50% in the other simulations, depending on the production yield of ONITR from ISOPO2+NO). The loss of isoprene nitrates occurs primarily by dry deposition (44% in BASE, and up to 48% in simulations using a slower loss rate with OH). Reaction with OH is responsible for 26% of the isoprene nitrate loss in BASE, and ~20% in simulations with slower reaction rate with OH.

Isoprene nitrates are shown to have a major impact on the NO_x budget in the summertime U.S. boundary layer. Based on the observational constraints, formation of isoprene nitrates consumes 17-21% of the emitted NO_x (17% "best guess" from BASE simulation). Of this amount, deposition of isoprene nitrates permanently removes 10-13% of NO_x emissions (10% best guess), 3-4% are exported (3% best guess), and 3-6% are recycled to NO_x (4% best guess).

While we used available observations to constrain uncertainties in isoprene nitrate chemistry, many uncertainties still exist and require further investigation. Our model budgets indicate that the reaction of isoprene with NO_3 is the major pathway for isoprene nitrate formation, but this pathway remains highly uncertain. The NO_3 pathway has not typically been considered important for isoprene because of the diurnal anticorrelation between isoprene (which peaks during mid-day) and NO_3 (which peaks at night). Since this pathway produces organic nitrates with a much higher yield than the OH pathway (assumed to be ~80% in our mechanism, versus 4-8% for the OH pathway), however, it can contribute significantly to isoprene nitrate production even though it is only a minor pathway for isoprene loss. We also find that our model results are highly sensitive to the degree of recycling of NO_x from the reaction of isoprene nitrates with OH. The amount of NO_x produced from this reaction, and the nature and fate of the multifunctional organic nitrates formed, need further investigation. Finally, the large discrepancy between simulated and observed ΣAN in the free troposphere suggests a shortcoming in the representation of nitrates in the model mechanism. Based on the available measurements, it is not yet known whether these "missing" nitrates are isoprene nitrates, or nitrates derived from other parent hydrocarbons.

References

Bey, I., D.J. Jacob, R.M. Yantosca, J.A. Logan, B.D. Field, A.M. Fiore, Q. Li, H.Y. Liu, L.J.
Mickley, and M.G. Schultz (2001), Global modeling of tropospheric chemistry with
assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, *106*,
23,073-23,095.

Chen, X., D. Hulbert, and P.B. Shepson (1998), Measurement of the organic nitrate yield from
OH reaction with isoprene, *J. Geophys. Res.*, *103*(D19), 25,563-25,568.

Choung B., and P. S. Steven (2002), Measurements of the kinetics of the OH-initiated oxidation
of isoprene, *J. Geophys. Res.*, *107*(D13), doi:10.1029/2001JD000865.

Day, D.A., P.J. Wooldridge, M. Dillon, J.A. Thornton, and R.C. Cohen (2002), A thermal
dissociation-laser induced fluorescence instrument for in-situ detection of NO_2,
peroxy(acyl)nitrates, alkyl nitrates, and HNO_3., *J. Geophys. Res.*, *107*(D6),
10.1029/2001JD000779.

Fan, J., and R. Zhang, Atmospheric oxidation mechanism of isoprene (2004), Environ. Chem., 1,
140-149, doi:10.1071/EN04045.

Fiore, A. M., L. W. Horowitz, D. W. Purves, H. Levy II, M. J. Evans, Y. Wang, Q. Li, and R. M.
Yantosca (2005), Evaluating the contribution of changes in isoprene emissions to surface

Erin Czech 8/15/06 1:54 PM
Deleted: 5/30/2006

ozone trends over the eastern United States, *J. Geophys. Res.*, *110*, D12303, doi:10.1029/2004JD005485.

Giacopelli, P., K. Ford, C. Espada, and P.B. Shepson (2005), Comparison of the measured and simulated isoprene nitrate distributions above a forest canopy, *J. Geophys. Res.*, *110*, D01304, doi:10.1029/2004JD005123.

Grossenbacher, J.W., et al. (2001), Measurements of isoprene nitrates above a forest canopy, *J. Geophys. Res.*, *106*(D20), 24,429-24,438.

Grossenbacher, J.W., et al. (2004), A comparison of isoprene nitrate concentrations at two forest-impacted sites, *J. Geophys. Res.*, *109*, D11311, doi: 10.1029/2003JD003966.

Guenther, A., C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman (1995), A global model of natural volatile organic carbon emissions, *J. Geophys. Res.*, *100*, 8873-8892.

Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. I. Palmer, C. Geron (2006), Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys. Discuss.*, *6*, 107-173.

Erin Czech 8/15/06 1:54 PM
Deleted: 5/30/2006

Horowitz, L.W., J. Liang, G.M. Gardner, and D.J. Jacob (1998), Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, *J. Geophys. Res.*, *103*, 13,451– 13,476.

Horowitz, L.W., et al. (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, *108*(D24), 4784, doi:10.1029/2002JD002853.

Houweling, S., F. Dentener, and J. Lelieveld (1998), The impact of non-methane hydrocarbon compounds on tropospheric photochemistry, J. Geophys. Res., 103, 10,673-10,696.

Kwok, E.S.C., and R. Atkinson (2005), Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update, *Atmos. Environ.*, *29*, 1685-1695.

Madronich, S., and S. Flocke (1998), The role of solar radiation in atmospheric chemistry, in *Handbook of Environmental Chemistry*, edited by P. Boule, pp. 1-26, Springer-Verlag, New York.

Nozière, B., I. Barnes, and K. Becker (1999), Product study and mechanisms of the reactions of α-pinene and of pinonaldehyde with OH radicals, *J. Geophys. Res.*, *104*(D19), 23,645-23,656.

Erin Czech 8/15/06 1:54 PM
Deleted: 5/30/2006

Paulson, S.E. and J.H. Seinfeld (1992), Development and evaluation of a photooxidation

mechanism for isoprene, *J. Geophys. Res.*, *97*, 20,703-20,715.

Pierce, T., C. Geron, L. Bender, R. Dennis, G. Tonnesen, and A. Guenther (1998), Influence of

increased isoprene emissions on regional ozone modeling, *J. Geophys. Res.*, *103*, 25,611-

25,629.

Pöschl, U., R. von Kuhlmann, N. Poisson, and P.J. Crutzen (2000), Development and

intercomparison of condensed isoprene oxidation mechanisms for global atmospheric

modeling, *J. Atmos. Chem.*, *37*, 29-52.

Purves, D.W., J.P. Caspersen, P.R. Moorcroft, G.C. Hurtt, and S.W. Pacala (2004), Human-

induced changes in U.S. biogenic VOC emissions: Evidence from long-term forest

inventory data, *Global Change Biol.*, *10*, 1-19, doi:10.1111/j.1365-2486.2004.00844.x.

Rosen, R.S., E.C. Wood, P.J. Wooldridge, J.A. Thornton, D.A. Day, W. Kuster, E.J. Williams,

B.T. Jobson, and R.C. Cohen (2004), Observations of total alkyl nitrates during Texas

Air Quality Study 2000: Implications for O_3 and alkyl nitrate photochemistry, *J.

Geophys. Res.*, *109*(D7), D07303, doi:10.1029/2003JD004227.

Shepson, P.B., E. Mackay, and K. Muthuramu (1996), Henry's law constants and removal

processes for several atmospheric β-hydroxy alkyl nitrates, *Enivron. Sci. Technol.*, *30*,

3618-3623.

Erin Czech 8/15/06 1:54 PM
Deleted: 5/30/2006

Shim, C., Wang, Y., Choi, Y., Palmer, P., Abbot, D., and Chance, K. (2005), Constraining global isoprene emissions with Global Ozone Monitoring Experiment (GOME) formaldehyde column measurements, *J. Geophys. Res.*, *110*(D24), D24301, doi:10.1029/2004JD005629.

Sprengnether, M., K.L. Demerjian, N.M. Donahue, and J.G. Anderson (2002), Product analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO, *J. Geophys. Res.*, *107*(D15), doi:10.1029/2001JD000716.

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld, and S.C. Liu (1987), Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature*, *329*, 705-707.

Treves, K., and Y. Rudich, The atmospheric fate of C_3-C_6 hydroxyalkyl nitrates (2003), *J. Phys. Chem. A*, *107*, 7809-7817.

Turquety, S., J.A. Logan, D.J. Jacob, R.C. Hudman, F.Y. Leung, C.L. Heald, R. M. Yantosca, S. Wu, L. K. Emmons, D.P. Edwards, and G.W. Sachse (2006), Inventory of boreal fire emissions for North America in 2004: The importance of peat burning and pyro-convective injection, submitted to *J. Geophys. Res.*.

Erin Czech 8/15/06 1:54 PM
Deleted: 5/30/2006

von Kuhlmann, R., M.G. Lawrence, U. Pöschl, and P.J. Crutzen (2004), Sensitivities in global

      scale modeling of isoprene, *Atmos. Chem. Phys.*, *4*, 1-17.

Wu, S., L.J. Mickley, D.J. Jacob, J.A. Logan, R.M. Yantosca, and D. Rind (2006), Why are there

      large differences between models in global budgets of tropospheric ozone?, submitted to

      J. Geophys. Res..

Erin Czech 8/15/06 1:54 PM
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Table 1. Isoprene mechanism used in base model simulations. Second-order reaction rate constants are given in units of molec^{-1} cm^3 s^{-1}.

Reaction	Rate Constant
ISOP + OH → ISOPO2	2.54E-11*exp(410/T)
ISOP + O3 → .4*MACR + .2*MVK + .07*C3H6 + .27*OH + .06*HO2 + .6*CH2O + .3*CO + .1*O3 + .2*MCO3 + .2*CH3COOH	1.05E-14*exp(-2000/T)
ISOP + NO3 → ISOPNO3	3.03E-12*exp(-446/T)
ISOPO2 + NO → .04*ONITR + .96*NO2 + HO2 + .57*CH2O + .24*MACR + .33*MVK + .38*HYDRALD	2.20E-12*exp(180/T)
ISOPO2 + NO3 → HO2 + NO2 + .6*CH2O + .25*MACR + .35*MVK + .4*HYDRALD	2.40E-12
ISOPO2 + HO2 → ISOPOOH	8.00E-13*exp(700/T)
ISOPO2 + CH3O2 → .25*CH3OH + HO2 + 1.2*CH2O + .19*MACR + .26*MVK + .3*HYDRALD	5.00E-13*exp(400/T)
ISOPO2 + CH3CO3 → CH3O2 + HO2 + .6*CH2O + .25*MACR + .35*MVK + .4*HYDRALD	1.40E-11
MVK + hv → .7*C3H6 + .7*CO + .3*CH3O2 + .3*CH3CO3	Photolysis
MVK + OH → MACRO2	4.13E-12*exp(452/T)
MVK + O3 → .8*CH2O + .95*CH3COCHO + .08*OH + .2*O3 + .06*HO2 + .05*CO + .04*CH3CHO	7.52E-16*exp(-1521/T)
MACR + hv → .67*HO2 + .33*MCO3 + .67*CH2O + .67*CH3CO3 + .33*OH + .67*CO	Photolysis
MACR + OH → .5*MACRO2 + .5*H2O + .5*MCO3	1.86E-11*exp(175/T)
MACR + O3 → .8*CH3COCHO + .275*HO2 + .2*CO + .2*O3 + .7*CH2O + .215*OH	4.40E-15*exp(-2500/T)

Reaction	Rate Constant
MACRO2 + NO → NO2 + .47*HO2 + .25*CH2O + .25*CH3COCHO + .53*CH3CO3 + .53*GLYALD + .22*HYAC + .22*CO	2.70E-12*exp(360/T)
MACRO2 + NO → ONITR	1.30E-13*exp(360/T)
MACRO2 + NO3 → NO2 + .47*HO2 + .25*CH2O + .25*CH3COCHO + .22*CO + .53*GLYALD + .22*HYAC + .53*CH3CO3	2.40E-12
MACRO2 + HO2 → MACROOH	8.00E-13*exp(700/T)
MACRO2 + CH3O2 → .73*HO2 + .88*CH2O + .11*CO + .24*CH3COCHO + .26*GLYALD + .26*CH3CO3 + .25*CH3OH + .23*HYAC	5.00E-13*exp(400/T)
MACRO2 + CH3CO3 → .25*CH3COCHO + CH3O2 + .22*CO + .47*HO2 + .53*GLYALD + .22*HYAC + .25*CH2O + .53*CH3CO3	1.40E-11
ISOPOOH + hv → .402*MVK + .288*MACR + .69*CH2O + HO2	Photolysis
ISOPOOH + OH → .5*XO2 + .5*ISOPO2	3.80E-12*exp(200/T)
MACROOH + OH → .5*MCO3 + .2*MACRO2 + .1*OH + .2*HO2	2.30E-11*exp(200/T)
ONITR + hv → HO2 + CO + NO2 + CH2O	Photolysis
ONITR + OH → .4*HYDRALD + .4*NO2 + HO2 + .6*XNITR	4.50E-11
ONITR + NO3 → NO2 + HO2 + XNITR	1.40E-12*exp(-1860/T)
ISOPNO3 + NO → 1.206*NO2 + .794*HO2 + .072*CH2O + .167*MACR + .039*MVK + .794*ONITR	2.70E-12*exp(360/T)
ISOPNO3 + NO3 → 1.206*NO2 + .072*CH2O + .167*MACR + .039*MVK + .794*ONITR + .794*HO2	2.40E-12
ISOPNO3 + HO2 → .206*NO2 + .794*HO2 + .008*CH2O + .167*MACR + .039*MVK + .794*ONITR	8.00E-13*exp(700/T)

Table 2. Sensitivity simulations.

Simulation	Yield[1]	Loss rate[2]	Deposition[3]	NO$_x$ recycling[4]
4% (BASE)	4%	Fast	Fast	40%
4%_slowOH	4%	Slow	Fast	40%
4%_slowDD	4%	Fast	Slow	40%
8%	8%	Fast	Fast	40%
8%_slowOH	8%	Slow	Fast	40%
8%_slowDD	8%	Fast	Slow	40%
4%_0%NOx	4%	Fast	Fast	0%
4%_100%NOx	4%	Fast	Fast	100%
8%_slowOH_100%NOx	8%	Slow	Fast	100%

[1]Yield of isoprene nitrates (ONITR) from the reaction of isoprene peroxy radicals (ISOPO2) with NO.

[2]Loss rates of ONITR. "Fast" indicates k(OH+ONITR) = 4.5×10^{-11} molec^{-1} cm^3 s^{-1}, J(ONITR) = J(CH$_3$CHO). "Slow" indicates k(OH+ONITR) = 1.3×10^{-11}, J(ONITR) = J(HNO$_3$).

[3]Rate of ONITR deposition. "Fast" indicates V$_d$(ONITR) = V$_d$(HNO$_3$), and H$_{298}$(ONITR) = 7.51×10^3 M atm^{-1}. "Slow" indicates V$_d$(ONITR) = V$_d$(PAN), and H$_{298}$(ONITR) = 7.51×10^2.

[4]Recycling of NO$_x$ from reaction of ONITR+OH. The balance of the reactive nitrogen produces multifunctional organic nitrates (XNITR).
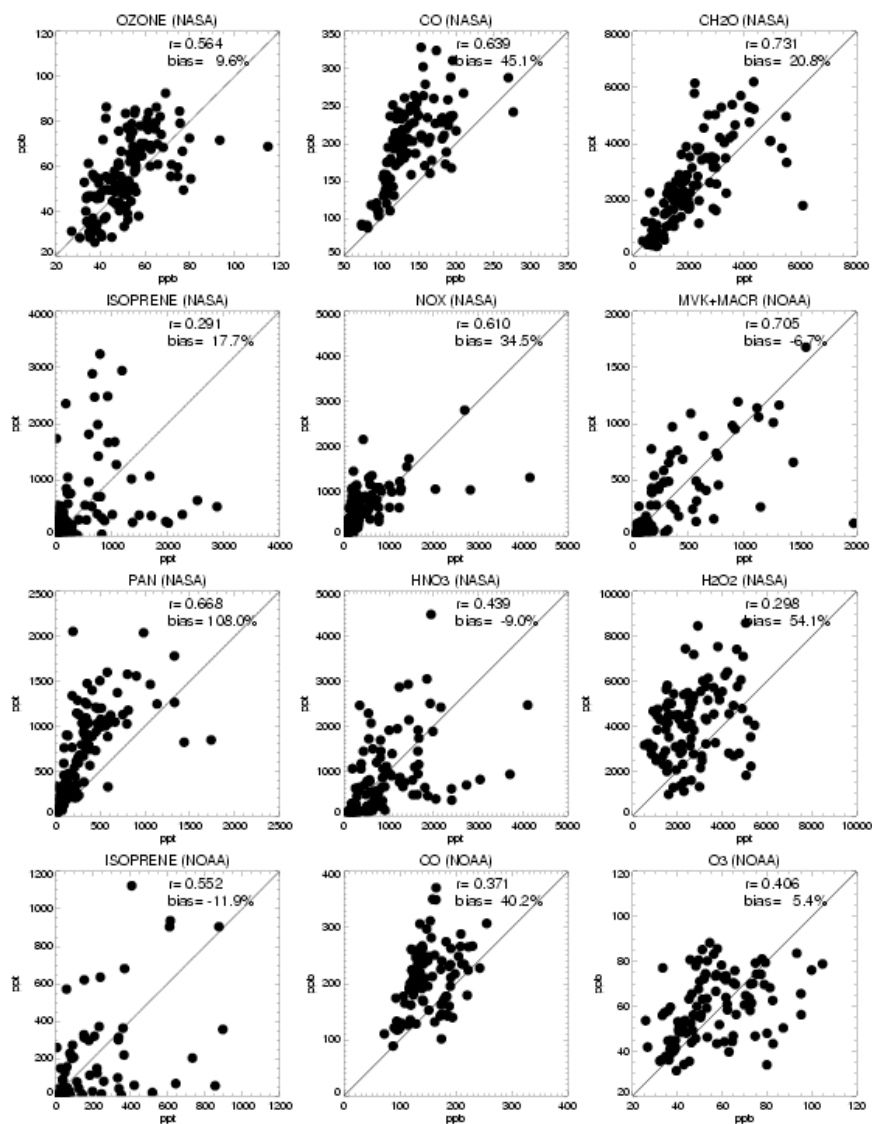
Figure Captions

Figure 1. MOZART-4 model versus observed concentrations of selected trace species for daytime observations (1500-2300 UTC) below 2 km. Hourly model results are sampled at the locations of 1-minute observations. The 1-minute model values and observations for each NOAA WP-3D and NASA DC-8 flight are then averaged onto the model grid. Observations shown from the NASA DC-8 are: ozone (Avery), CO (Sachse), CH_2O (Fried), isoprene (Blake), NO_x = NO (Brune) + NO_2 (Cohen), PAN (Singh), HNO_3 (Wennberg), and H_2O_2 (Wennberg). Observations shown from the NOAA WP-3D are: methylvinyl ketone + methacrolein (MVK+MACR, de Gouw and Warneke), isoprene (de Gouw and Warneke), CO (Holloway), and ozone (Ryerson).

Figure 2. Vertical profile of the sum of all alkyl nitrates (ΣAN) from observations (black) and model (colored by simulation as shown in legend) from all ICARTT DC-8 flights (left). Correlation plot of ozone versus ΣAN and reduced major axis regression line from observations (black points and line) and model (colored points and lines) for daytime (1500-2300 UTC) DC-8 data over the eastern United States (24-52°N, 62.5-97.5°W).

Figure 3. Budgets of isoprene nitrates in the eastern United States (24-52°N, 62.5-97.5°W) boundary layer (below 800 hPa) during July 2004 for each model simulation. Production of isoprene nitrates occurs from terpenes (pinene), methylvinyl ketone and methacrolein (MACR), and from isoprene reactions with NO3 (NO3) and OH (ISOP). Loss occurs via photolysis and vertical diffusion (hv+DIF), reaction with OH (OH), wet deposition (WD), advection (ADV),

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convection (CNV), and dry deposition (DD).

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Larry W. Horowitz 5/24/06 9:11 AM
Comment: Should more information be included on the instruments / measurement technique? References to ICARTT instrument papers?

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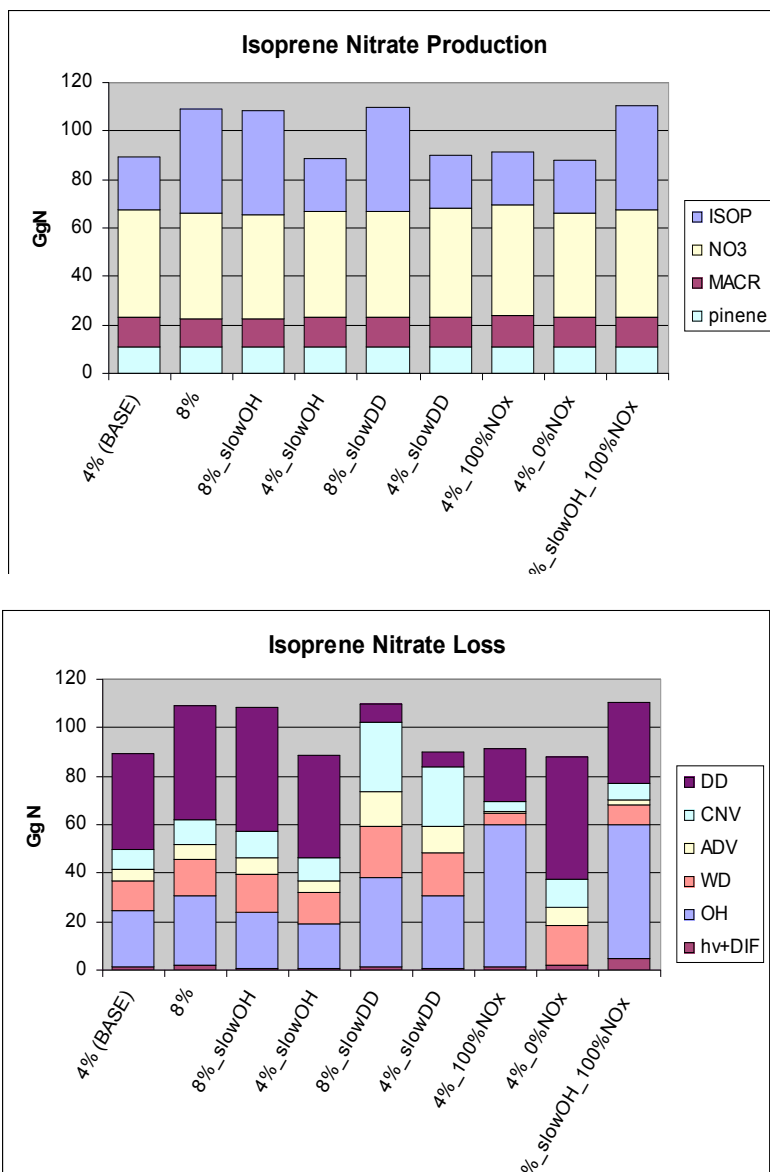
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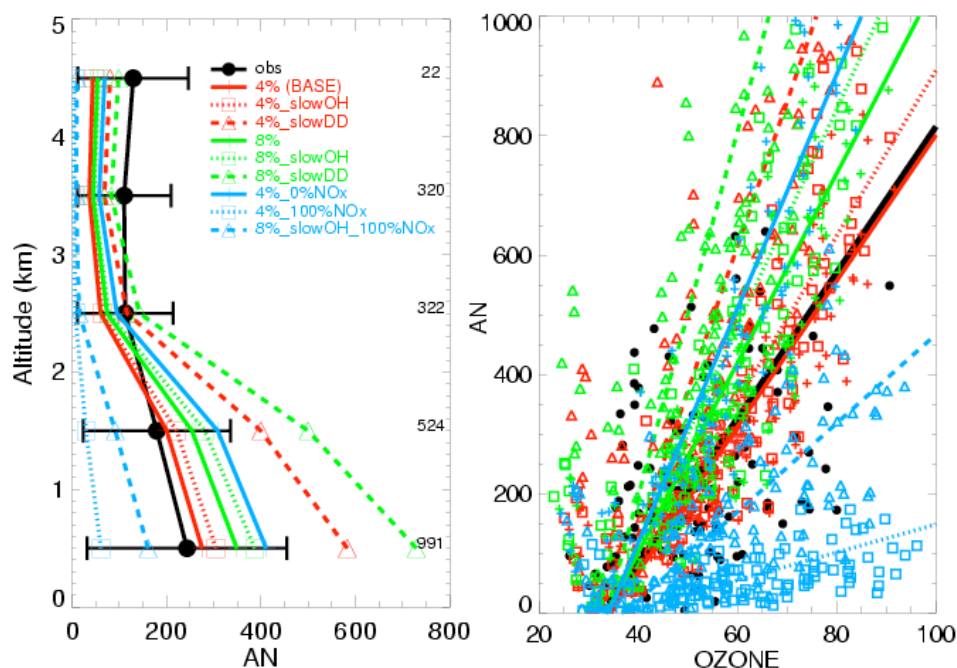
Figure 3. Mean ICARTT vertical profile of the sum of all alkyl nitrates (ΣAN) from observations (black, standard deviations indicated by horizontal bars) and model (colored by simulation as shown in legend; see also Table 2) from all DC-8 flights (left). Correlation plot of ozone versus ΣAN and reduced major axis regression line from observations (black points and line) and model (colored points and lines) for daytime (1500-2300 UTC) DC-8 data over the eastern United States (24-52°N, 62.5-97.5°W) (right). Model values and observations are sampled every minute.